

Method for Regenerating Support Catalysts Coated with Gold Particles for the Oxidation of Unsaturated Hydrocarbons
FIELD OF THE INVENTION

This invention relates to a method of regenerating catalysts for the catalytic production of epoxides from unsaturated hydrocarbons by oxidation with molecular oxygen in the presence of molecular hydrogen in the gas phase, and also relates to the use of these regenerated catalysts for the oxidation of unsaturated hydrocarbons.

BACKGROUND OF THE INVENTION

The direct oxidation of unsaturated hydrocarbons with molecular oxygen in the gas phase does not normally proceed below 200°C - even in the presence of catalysts, and it is therefore difficult selectively to produce oxidation products which are susceptible to oxidation, such as epoxides, alcohols or aldehydes for example, since subsequent reactions of these products frequently proceed more rapidly than the oxidation of the olefines themselves which are used.

As an unsaturated hydrocarbon, propene oxide constitutes one of the most important basic chemicals of the chemical industry. More than 60 % of this substance is used in the plastics sector, particularly for the production of polyether polyols for the synthesis of polyurethanes. In addition, propene oxide derivatives have an even larger share of the market in the field of glycols, particularly for lubricants and antifreeze compositions.

World-wide, about 50 % of propene oxide is currently synthesised by the "chlorohydrin method". The other 50 % is obtained by "oxirane methods", and this trend is increasing.

In the chlorohydrin method (F. Andreas et al.; Propylenchemie, Berlin 1969), the chlorohydrin is first formed by the reaction of propene with HOCl (water and chlorine), and propene oxide is subsequently formed from the chlorohydrin by the separation of HCl with lime. This method is costly, but when it is optimised appropriately it provides a high selectivity (>90 %) at high conversions. Chlorine losses in the chlorohydrin method, in the form of valueless calcium chloride or

"Express Mail" mailing label number EK983331152US
Date of Deposit July 27, 2000

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Donna J. Veatch

(Name of person mailing paper or fee)

Donna J. Veatch
Signature of person mailing paper or fee)

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sodium chloride solutions, have hitherto led to a search for oxidation systems which are free from chlorine.

- Instead of the inorganic oxidising agent HOCl, organic compounds have been selected for the transfer of oxygen to propene (oxirane method). This indirect epoxidation is based on the fact that organic peroxides such as hydroperoxides or peroxy-carboxylic acids in the liquid phase are capable of selectively transferring their peroxide oxygen to olefines with the formation of epoxides. In the course of this process, hydroperoxides are converted into alcohols and peroxy-carboxylic acids are converted into acids. Hydroperoxides and peroxy-carboxylic acids are produced from the corresponding hydrocarbon or aldehyde, respectively, by autoxidation with air or molecular oxygen. One serious disadvantage of indirect oxidation is the economic dependence of the value of propene oxide on the market value of the coupled product.
- Using titanium silicate (TS 1) as a catalyst (Notari et al., US 44 10 501 (1983) and US 47 01 428) it proved possible for the first time to epoxidise propene with hydrogen peroxide in the liquid phase under very mild reaction conditions with selectivities > 90 % (Clerici et al., EP-A 230 949).
- The oxidation of propene by a gas mixture consisting of molecular oxygen and molecular hydrogen proceeds with a low yield in the liquid phase over titanium silicates containing platinum metal (JP-A 92/352771).

- The direct gas phase oxidation of propene to form propene oxide with a selectivity of 100 % was described for the first time in EP-A 0 709 360 A1 (Haruta et al.). This is a catalytic gas phase oxidation with molecular oxygen in the presence of the reducing agent hydrogen. A special titanium dioxide comprising an anatase modification which is coated with nanometre-scale gold particles is used as the catalyst. The maximum propene conversion and yield are quoted as 1 %. The Au/TiO₂ catalysts described achieve a propene conversion of about 1 % for a very short time only. Typical half-lives at moderate temperatures (40-50°C) are only 100-200 minutes, for example.

The regeneration of catalysts which are coated with gold and which are based on titanium silicate by dilute hydrogen peroxide solution was known hitherto (Thiele et al., J. Mol. Cat. 117, pages 351-356, 1997).

- 5 The possibility of efficiently regenerating the catalyst is of decisive importance for the development of a propene oxidation process which is of economic interest.

DETAILED DESCRIPTION OF THE INVENTION

- 10 It has surprisingly been found that when catalysts which have become inactive are treated with water, dilute acids or dilute hydrogen peroxide solution, catalytic activities of up to 80 % of the original activity can be achieved again. The catalysts which have become inactive are preferably washed with dilute acids (e.g. dilute H_2SO_4 or HF) at a pH of 4 to 7.5, preferably 5.5 to 6.

- 15 The present invention therefore relates to a method of regenerating support catalysts, which are coated with gold particles and which are based on titanium dioxide or hydrous titanium dioxide, for the oxidation of unsaturated hydrocarbons in the gas phase, wherein the catalytic activity of the catalyst is regenerated by bringing it into contact with water or with dilute acid or with a dilute hydrogen peroxide solution.

- 20 Treatment in the sense of the present invention can be effected at room temperature or at elevated temperature. In variants of the invention, elevated pressures and/or the use of steam can advantageously be put into effect.

- 25 Treatment can be effected separately after removing the catalyst from the reactor, or can also be effected in the reactor if the catalytic oxidation of propene in the presence of hydrogen and regeneration of the catalyst with water or hydrogen are caused to proceed cyclically in succession. In one embodiment of this variant, it is advantageous to perform the operations of catalysis and regeneration simultaneously in a plurality of spatially separated reactors which are connected in series. These phases can be
30 connected so that they operate alternately.

Agitation of the regeneration mixture may be advantageous, but is not a requirement of the use according to the invention.

According to the invention, support catalysts can be regenerated which are coated with nanometre-scale gold particles and which are based on titanium dioxide or hydrous titanium oxide. These catalysts are preferably produced by the "deposition-precipitation" method.

The concentration of dilute hydrogen peroxide solution is usually within the range from 1 to 10 % by weight, preferably 1 to 4 % by weight.

When catalysts which are regenerated according to the invention are used for the oxidation of unsaturated hydrocarbons, there is no restriction on the amount of catalyst which is used and on the amounts of gases which are used. The "space velocity" of the gas stream through the catalyst bed should usually amount to about 0.5 to 20 l/g catalyst per hour.

The use according to the invention of regenerated catalysts is effected in the presence of the gases oxygen and hydrogen. In the presence of these gases at 150°C, the oxygenated products propene oxide and acetone are also formed in addition to the main products comprising water, propane and CO₂. If the reaction temperature is reduced to <100°C, preferably to 30-60°C, the formation of water is suppressed considerably, and the formation of CO₂ is suppressed completely. At a temperature between 30 and 60°C only traces of the other components (about 1 % with respect to propene oxide) are found in addition to the main product propene oxide (yield about 4-5 %). The proportion of water is twice the proportion of propene oxide (molar basis).

The composition of the gas phase, which contains propene, oxygen, hydrogen and possibly an inert gas, is not only important as regards the space-time yield, but is also important as regards safety. In theory, all molar compositions of the gases propene / oxygen / hydrogen / nitrogen / inert gas (e.g. nitrogen) can be used. The preferred gas ratios for the oxidation of propene are the following ratios: H₂ / hydrocarbon / oxygen / nitrogen: 20-80 % / 10-50 % / 1-10 % / 0-50 %; the preferred H₂ / hydrocarbon / oxygen / nitrogen ratio is 30-75 % / 15-40 % / 3-8 % / 0-10 %. The molecular oxygen

which is used for the reaction can originate from diverse sources, e.g. pure oxygen, air or other oxygen/inert gas mixtures.

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Examples

Direct oxidation of propene to propene oxide

- 5 **Standard reaction conditions:** the reactor was a fixed bed tubular reactor (diameter 1 cm, length 20 cm) made of double-walled glass, which was heated at a controlled temperature of 46°C by means of a water thermostat. A static mixing and temperature control section was disposed upstream of the reactor. The gold-support catalyst was placed on a glass frit beforehand. The catalyst loading was 1.8 l/g catalyst/hour. The
- 10 gaseous starting materials were metered into the reactor from top to bottom by means of mass-flow controllers. The ratios of the gaseous starting materials corresponded to $O_2 / H_2 / C_3H_6 = 0.1 / 1.3 / 0.4$ l/hour. The reaction gas mixture was analysed by gas chromatography using an FID detector (for all organic compounds containing oxygen, with the exception of CO_2) and a thermal conductivity detector (for permanent gases,
- 15 CO , CO_2 and H_2O). The apparatus was controlled via a central data recording system.

The gold particle size of all the catalysts was investigated by TEM (transmission electron microscopy).

20 **Catalyst preparation 1**

- 100 mg $H(AuCl_4)$, dissolved in 100 ml of deionised water, were added drop-wise over 60 minutes at room temperature, with stirring, to a suspension of 10 g hydrous titanium oxide (BET specific surface $380 \text{ m}^2/\text{g}$, sulphate content 0.6 %, 12 % water)
- 25 in 0.3 l of deionised water. The pH was adjusted to 8 with an 0.5 molar Na_2CO_3 solution in order to precipitate gold hydroxide. The slightly yellow suspension was decolorised. The suspension was stirred for 3 hours at room temperature, and the solid was separated and washed 4 times with 25 ml of deionised water each time. The solid was dried for 2 hours at 150°C and for 1 hour at 200 °C, and the dried contact catalyst
- 30 was subsequently calcined in air for 2 hours at 250°C and for 5 hours at 400°C.

A catalyst which contained 0.5 % by weight gold was obtained. Characterisation by TEM showed the presence of nanometre-scale gold particles with average particle

diameters of about 1-6 nm. The results of the catalytic reaction in accordance with the standard reaction conditions (Example A) are given in Table 1.

Catalyst preparation 2:

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A solution of 0.104 g $\text{HAuCl}_4 \times \text{H}_2\text{O}$ in 400 ml distilled water was heated to 70°C and adjusted to pH 7.5 with an aqueous 0.1 N NaOH solution. 5 g titanium dioxide (an anatase-rutile mixed oxide; P 25 supplied by Degussa) was added in one portion with intensive stirring, and the batch was stirred for a further 1 hour. The solid was washed 10 5 times with 3 litres of distilled water each time, dried under vacuum at room temperature for 12 hours, and calcined for 4 hours at 400°C. A gold-titanium dioxide catalyst was obtained which contained 1 % by weight gold.

The results of the catalytic reaction in accordance with the standard reaction 15 conditions (Example B) are given in Table 1.

Examples 1 to 10

Catalyst regeneration and catalytic activity of gold support catalysts which had become inactive and which were treated according to the invention with water, dilute acids or dilute hydrogen peroxide solutions:

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Example 1

A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide 25 yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H_2O , stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

30 The results of the catalytic reaction are given in Table 1.

Example 2

5 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H₂O, stirred for 1 hour at 80°C, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

Example 3

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A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H₂O, stirred for 3 hours at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for
15 the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

Example 4

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A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml of 3 % H₂O₂ solution, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained
25 was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

Example 5

5 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml of 6 % H₂O₂ solution, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

Example 6

15 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml of 3 % H₂O₂ solution, stirred for 1 hour at 50°C, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

Example 7

25 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H₂O which had been adjusted with 0.05 molar H₂SO₄ to pH 6, was stirred for 3 hours at room temperature, separated, dried for 1 hour at 150°C and calcined for 2 hours at 400°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

Example 8

5 A catalyst which had become inactive due to reaction (2 g; 0.6 % propene oxide yield), and which had been produced according to *catalyst preparation 1*, was suspended in 100 ml H₂O which had been adjusted with 0.05 molar H₂SO₄ to pH 6.5, was stirred for 3 hours at room temperature, separated, dried for 1 hour at 150°C and calcined for 2 hours at 400°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

10 **Example 9**

15 A catalyst which had become inactive due to reaction (2 g; 0.2 % propene oxide yield), and which had been produced according to *catalyst preparation 2*, was suspended in 500 ml water, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

20 **Example 10**

25 A catalyst which had become inactive due to reaction (2 g; 0.2 % propene oxide yield), and which had been produced according to *catalyst preparation 2*, was suspended in 100 ml of 3 % H₂O₂ solution, stirred for 1 hour at room temperature, separated, and dried for 1 hour at 150°C. The contact catalyst which was thus obtained was used for the oxidation of propene by the standard procedure.

The results of the catalytic reaction are given in Table 1.

Table 1

Catalyst preparation 1	Time (min)	Propene oxide yield (%)	Propene oxide selectivity (%)
Example A (active)	30	5.3	>97
Example A (inactive)		0.6	>97
Example 1	30	3.7	>97
Example 2	30	3.8	>97
Example 3	30	3.8	>97
Example 4	30	3.9	>97
Example 5	30	3.6	>97
Example 6	30	3.8	>97
Example 7	30	4.2	>97
Example 8	30	4.0	>97

Catalyst preparation 2	Time (min)	Propene oxide yield (%)	Propene oxide selectivity (%)
Example B (active)	30	1.4	>97
Example B (inactive)		0.2	>97
Example 9	30	0.9	>97
Example 10	30	1.0	>97

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